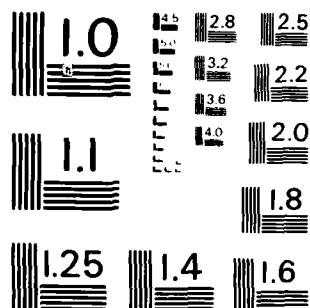


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Proposed future space-based beam weapons systems will most probably require an intense neutral particle beam for effective operation across geomagnetic field lines. Such neutral particle beams can most efficiently be obtained by stripping excess electrons from negative ion beams. The detailed physics of negative ion production is not well understood. The physics of present production techniques must be studied and new techniques developed in order to obtain intense negative ion beams. The objective of this work is to study the process of dissociative attachment of electrons. Specifically, to measure the cross sections for polar,		

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20. dissociation and dissociative attachment for production of H^- . It is suspected that these dissociative attachment cross sections for the production of H^- from alkali hydrides are large. The insight gained from this study will be extremely helpful in the fabrication of high current density H^- beam sources for use in the production of intense neutral hydrogen beams. A selection of alkali hydride molecules will be investigated in order to determine the largest cross sections for the production of H^- by electron impact. The angular distribution of the H^- ions will be measured. An optimal vapor pressure for the efficient production of H^- will be found. The feasibility of extending the proposed research to the deuterium bearing molecule will be determined.

The following progress has been made:

One instrument, representing state of the art, has been built. It is dedicated to the measurement of dissociative electron attachment and ionization cross sections for molecules of interest in the field of opening and closing of high current and high voltage gas phase switches and in the generation of intense beams of neutral particles. A new method has been developed to obtain absolute values of dissociative attachment cross sections in a cross beam collision geometry. A beam forming high temperature furnace has been fabricated for generating a beam of molecules which are normally found in solid phase at room temperature. Cross sections for the generation of the various negative ions by dissociative electron attachment have been measured for the following molecules: $SO(2)$, $H(2)O$, HCl , and LiH . A new technique for the measurement of dissociative attachment cross sections from the vibrationally excited molecules has been developed.

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PRODUCTION OF NEGATIVE IONS BY ELECTRON IMPACT

Principal Investigator: S. K. Srivastava

AFOSR-ISSA-82-00009

A final report for the work performed during the first phase of the research. (Period: May 1981 to Oct. 31, 1982)

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Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91109

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I. A BRIEF SUMMARY OF THE WORK DONE

The financial grant for the proposed work began in May, 1981. Since then the following progress has been made:

- One instrument, representing state of the art, has been built. It is dedicated to the measurement of dissociative electron attachment and ionization cross sections for molecules of interest in the field of opening and closing of high current and high voltage gas phase switches and in the generation of intense beams of neutral particles. A photograph of this instrument is shown in Figure 1. Detailed description is given in Section II.
- A new method has been developed to obtain absolute values of dissociative attachment cross sections in a cross beam collision geometry. It is explained in Section II.
- A beam forming high temperature furnace has been fabricated for generating a beam of molecules which are normally found in solid phase at room temperature. A photograph of this furnace is shown in Fig. 2. It will be described in detail in Section II.
- Cross sections for the generation of the various negative ions by dissociative electron attachment have been measured for the following molecules: SO_2 , H_2O , HCl , and LiH . Data have been supplied to modelers. Details are presented in Section III.
- A new technique for the measurement of dissociative attachment cross sections from the vibrationally excited molecules has been developed. It will be described in detail in Section IV.

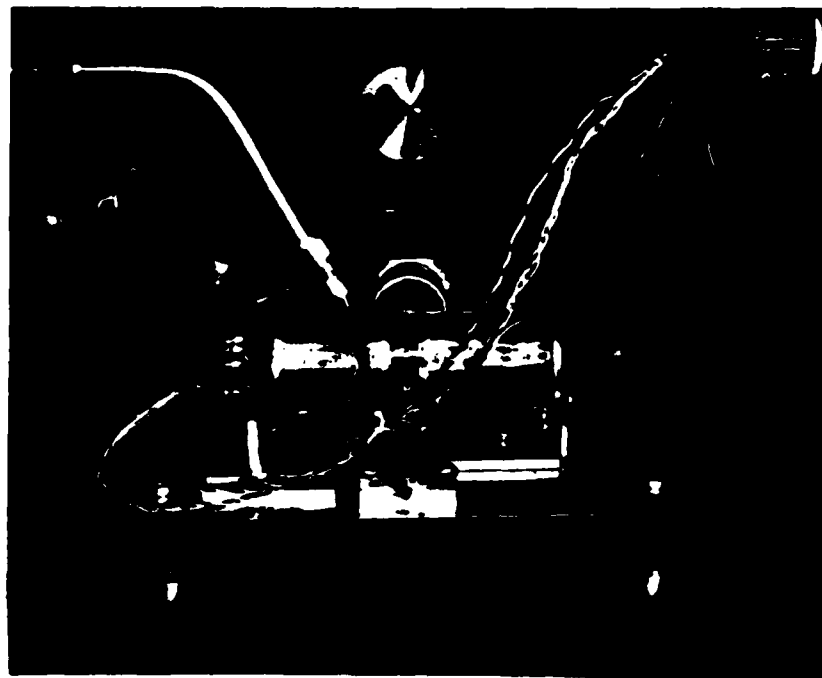


Fig. 1



Fig. 2

- Three papers have been submitted for publication. They are attached with this report. Four additional papers are in preparation at the present time. Three papers have been presented in an international meeting.
- An invited talk related to the present research has been given in the "United State/Japan Seminar on Electron-Molecule Collisions and Photoionization Processes, 26-29 October, 1982". A copy of the abstract is attached with this report.

II. DESCRIPTION OF THE INSTRUMENTS AND METHOD FOR CALIBRATION

For the purpose of a systematic study of the process of dissociative attachment of electrons with the molecules an instrument was fabricated. This instrument contains a mass spectrometer for the mass analysis of dissociated fragments. The detailed description of this instrument is given in the following.

1) DISSOCIATIVE ATTACHMENT SPECTROMETER:

A schematic diagram of the apparatus is shown in Fig. 3. It utilizes a crossed electron beam-molecular/atomic beam collision geometry. In the case of gases, the beam of atoms or molecules is produced by flowing the gas through a capillary array. Alternatively, in the case of species which are solids or liquids at room temperature an electron bombarded oven or a resistance heated oven¹ is utilized to produce the target beam. The beam of electrons is generated by heating a pure tungsten filament. The electrons are first extracted from the filament and are then accelerated or decelerated by three cylindrical lenses. This beam is collimated by the help of an axial \vec{B} field which is produced by a solenoid within which the electron gun and a Faraday cup are housed. The solenoid produces the B field of the order of 200 gauss.

The present beam of electrons is energy unselected. An energy profile of this beam was obtained by utilizing the retarding potential on the Faraday cup. It is found that the full width at half maximum (FWHM) is approximately 300 meV. The energy of the electrons is varied by changing the bias on the filament with respect to the last electrode of the electron gun. This electrode is kept at ground (earth) potential. It was found that the beam current, as measured by the Faraday cup, remained constant as the energy of the beam was changed from 0.5 eV to about 10 eV which is the energy range of the present interest. Although the energy of

DISSOCIATIVE IONIZATION AND ATTACHMENT SPECTROMETER (DIMENSIONS NOT TO SCALE)

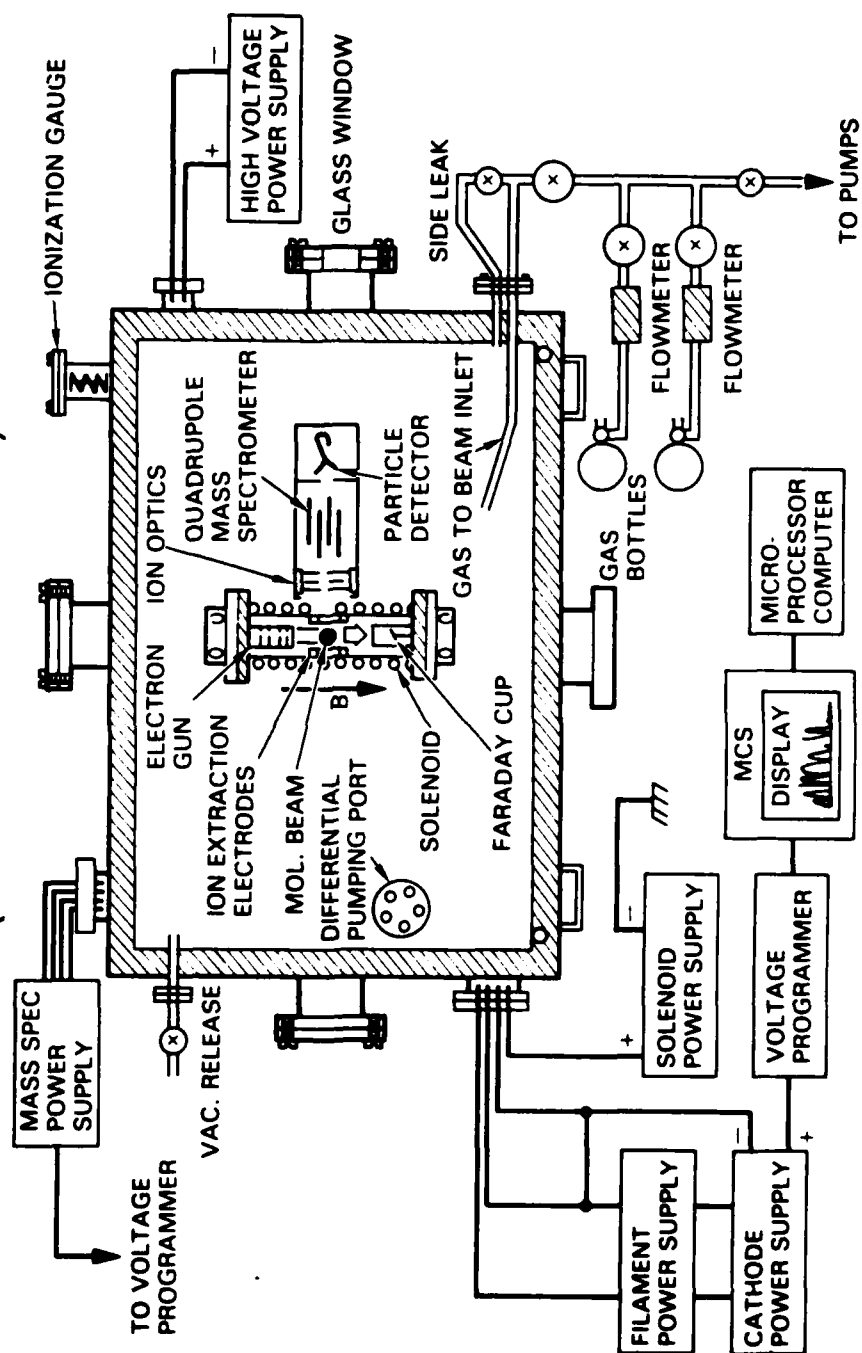


Fig. 3

the electron beam can be obtained by recording the filament bias voltage, the contact potentials at various surfaces tend to change it from its actual value. In the present work the energy of the beam was calibrated by utilizing the previously measured peak values of electron attachment energies for H^-/H_2 ,² O^-/O_2 ³ and O^-/CO_2 .⁴ It was found that the filament bias voltage needed a correction of +0.5 volts to get the true energy of the electron beam.

The negative ions produced by attachment of electrons to the target molecules are extracted out of the \vec{B} field by two parallel molybdenum wire meshes between which a voltage is applied. This voltage produces a homogeneous electric field with a gradient of 3 to 10 V/cm at the target. The direction of the field is normal to both electron beam and molecular beam. One grid is biased negative with respect to the ground and the other positive. The molecular beam is kept at ground potential. It was found that this arrangement did not disturb the electron beam. The efficiency of extraction of ions was measured by changing the extracting electric field from 0 up to 10 V/cm. It was found that by increasing the electric field strength, the detected ion intensity increased rapidly in the beginning. However, at about 3 eV and above the ion intensity became almost constant as a function of the field strength. This indicated that the measured ion current did not depend on the initial energy and angular distribution of the ions. All our measurements were performed in this region of extracting voltage. The extracted negative ions are accelerated from 0 to 200 V/cm and focused at the entrance aperture of a quadrupole mass spectrometer by an ion lens (Fig. 3). This mass spectrometer can measure up to about 80 amu and has a resolution of approximately 1 amu. The mass analyzed ions are accelerated by a 3.2 KV potential and are detected by a spiraltron multiplier. Each negative ion is counted as an event by a multichannel scaler.

A vacuum of about 10^{-8} Torr was obtained when the gas forming the molecular beam was not flowed into the vacuum chamber. However, the pressure rose to about 10^{-7} Torr when the molecular beam was on.

The procedure for obtaining the resonance energies is as follows. First, the mass spectrometer is set to detect the mass of interest. Then, the electron energy is varied. The output signal from the spiraltron is recorded by a multichannel scaler as a function of electron energy. This process is repeated several times until sufficient signal to noise ratio is obtained. The variation of ion intensity as a function of energy usually shows a maximum.

The relative intensities of negative ions of various masses give the values of relative cross sections. These cross sections, in turn, are the measures of relative efficiencies for the production of the various species by dissociative attachment. However, in order to get the true values of relative intensities one has to know the values of mass dependent transmission efficiencies of the ion optics, the quadrupole mass spectrometer and the charged particle detector. The determination of these efficiencies will be described at the end of this section.

11) METHOD FOR OBTAINING ABSOLUTE VALUES OF CROSS SECTIONS:

In order to obtain the absolute values of the cross sections, the relative flow technique⁸ developed in our laboratory for collision cross section measurements was utilized. This technique employs a measurement of the ratio of the intensity of the negative ions of the unknown species (for example, O^-/SO_2 , S^-/SO_2 , SO^-/SO_2) to that of from O^-/O_2 . At the same time, the flow rates behind the capillary array⁸ are measured. First, the gas whose dissociative attachment cross section has to be measured is flowed through the capillary array and a beam is formed. The negative ion intensity $I(B^-)$ is then measured. Subsequently, the

gas AB is turned off and O_2 is flowed through the capillary array. The negative ion current $I(O^-)$ is again recorded. Providing that the measurement is performed under the conditions of molecular flow through the capillary array, the following relation is used to obtain the cross section:

$$\sigma(B^-/AB) = \sigma(O^-/O_2) \frac{I(B^-)}{I(O^-)} \left[\frac{m(O_2)}{M(AB)} \right]^{\frac{1}{2}} \cdot \frac{N(O_2)}{N(AB)} \cdot K \quad (1)$$

where $m(AB)$ and $m(O_2)$ are molecular weights of respective gases, $N(O_2)$ and $N(AB)$ are the flow rates of the two gases through the capillary array and K is a calibration constant which determines the transmission efficiency of the ion optics, quadrupole mass spectrometer and charged particle detector for B^- and O^- .

Calibration constant K for the various masses was experimentally obtained by assuming that the transmission efficiency of the ion optics, quadrupole mass spectrometer and charged particle detector do not depend upon the charge of the particle. Thus, the values of K should be the same for B^+ as for B^- or for O^+ as for O^- . We chose gases whose ionization cross sections are well known. These are $(H^+/H_2)^4$, $(He^+/He)^5$, $(O^+/O_2)^4$, $(Ne^+/Ne)^5$, $(Ar^+/Ar)^5$ and $(Kr^+/Kr)^5$. Utilizing equation (1) and changing in it all negative signs into positive signs one obtains an equation for positive ion cross sections. Since all the quantities in this equation are either known or can be obtained experimentally for the two gases out of the ones mentioned above except K the values of K for various mass numbers ranging from H to Kr can be calculated. We followed this method for calibrating our instrument. The calibration constant K (relative efficiency) as a function of the mass number is a bell shaped curve shown in Fig. 4. The relative efficiency is increasing with the mass number up to about mass number 45, then it is decreasing at higher mass number. Our results are in agreement with Ehlert's measurements⁶

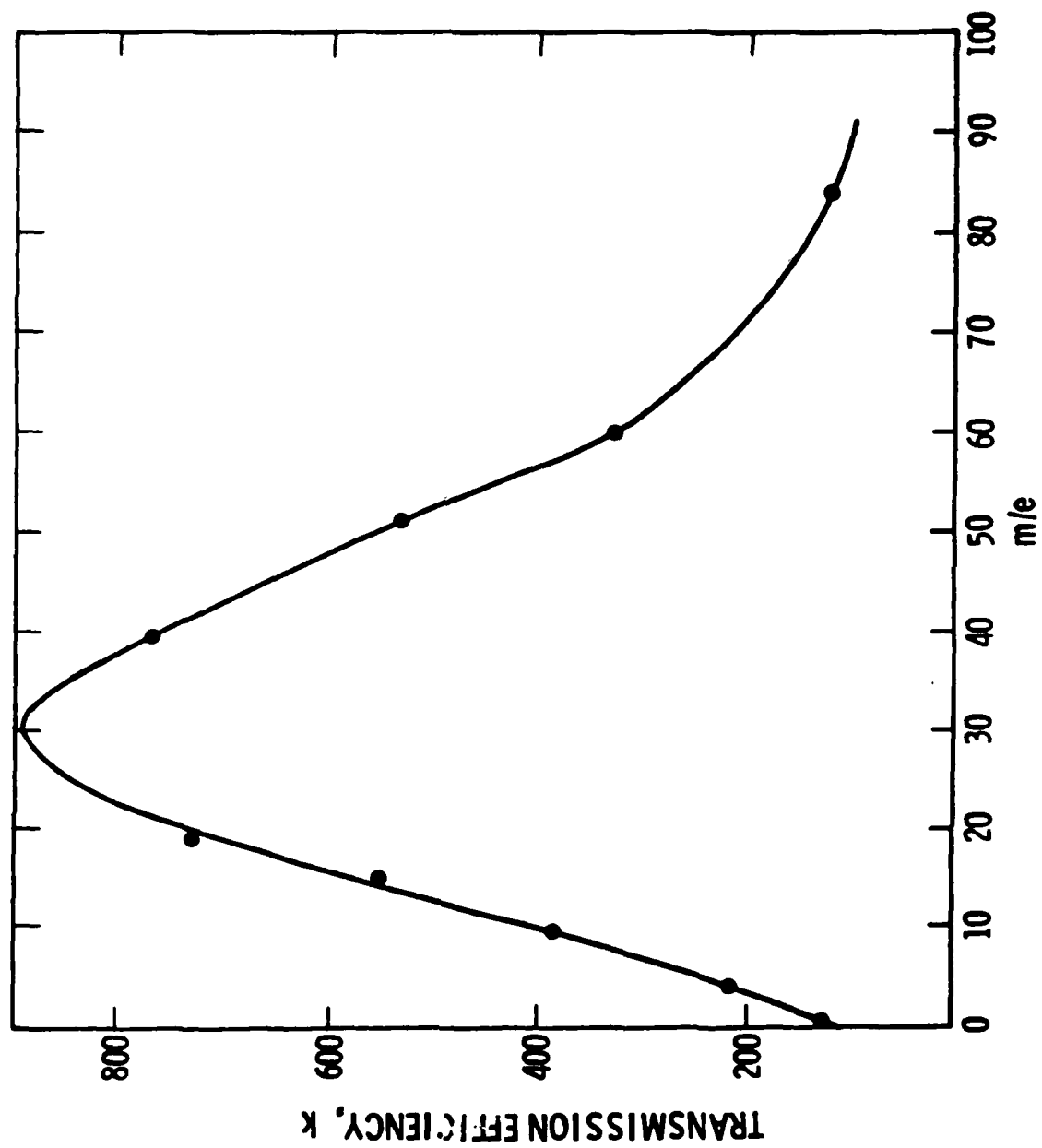


Fig. 4

(full curve, Fig. 4). We have checked our results in the case of negative ions using the well known dissociative electron attachment cross sections of $[H^-/H_2]^6$ and $[O^-/O_2]^7$. Taking into account our 5% error in measurements, the relative efficiency value in the case of negative and positive ions are equal, i.e., $K(\frac{O^-}{H^-}) = K(\frac{O^+}{H^+})$.

The contribution of the background scattering (both direct beam contribution and scattering by the background gas) to the scattering from the target gas beam is measured by providing an alternate leak to the vacuum chamber (see Fig. 3). The flow to the chamber is switched from the capillary array to the alternate gas inlet and the proper background pressure for the desired gas is established. The mass selected beam intensity is then measured as a function of the electron beam energy. It is found that the maximum value of the background scattering is about 5%. Thus, by using the side leak we have obtained background signal to correct the final results reported in the next section.

111) HIGH TEMPERATURE BEAM FORMING FURNACE:

There are certain substances of present interest which exist in the solid phase at room temperature. For example, LiH is a solid at room temperature. We proposed to study this molecule. In order to form a molecular beam, the substance has to be heated in a crucible to the temperature where the solid substance effuses in the form of a beam through a hole in the crucible. Figure 2 shows a photograph of an arrangement which was fabricated for the purpose of generating a beam of LiH.

The basic components of the high temperature crucible arrangement are:

a) a tantalum or a stainless steel crucible which is one half inch in diameter and 1.5 inch in height. This crucible has a 0.25 inch long and about 0.1 inch diameter snout at the top from where the substance effuses to form a beam. The crucible is either heated by the electron bombardment or by a coaxial heating wire.

With this arrangement a temperature of about 1000°C is easily achieved.

b) a reflective shield made out of a copper cylinder 2.5 inches in diameter and 4.5 inches in height with a 0.5 inch opening at the top. Around this cylinder copper tubing is wrapped through which chilled water is flowed to cool the rest of the structure on which the crucible sits.

c) a base with insulators to isolate the electrical connections.

d) a calibrated thermocouple for monitoring the temperature of the crucible.

III. CROSS SECTION DATA

Absolute values of dissociative attachment cross sections for SO_2 , CO_2 , H_2O , LiH and HCl have been obtained by utilizing a new technique (described in Section II) developed during the progress of the present work. In the following detailed results will be given for each molecule.

SO_2 : After the negative ion spectrometer described in Section II was built SO_2 was the first molecule for which the cross sections were measured. This choice was based on two reasons. First, it is known that the cross sections for the production of O^- from SO_2 is large. This is important from the point of view of the neutral beam research which is the aim of the present task. Second, the resonance electron energies at which the dissociation takes place are just right for using SO_2 in the development of a high current and high voltage switch.⁹ The data on the cross section were supplied to Prof. M. Kristiansen's group in Texas Tech, Lubbock for further evaluations by putting them into their models. Table I of the preprint #1 by O. J. Orient and S. K. Srivastava attached with this report gives the absolute values of cross sections. This was the first measurement of such cross sections for SO_2 by crossed electron beam-molecular beam technique. These cross sections have been determined with an accuracy of $\pm 15\%$.

The present instrument has the capability of measuring dissociative ionization cross sections too. Therefore, these cross sections were measured for SO_2 . They are given in Table I of the preprint #2 by O. J. Orient and S. K. Srivastava attached with this report.

LiH : Wong and his associates¹⁰ found that when the NaH powder is irradiated by a beam of CO_2 laser H^- ion current of about 10A was produced. This finding appeared to be very promising for the development of a source which could produce

intense neutral beams of H^- ions by laser irradiation. Wong and his associates explained the production of H^- from NaH on the basis of Saha equation:

$$N_H = \lambda^3 N_e N_0 \exp(E_-/kT_e), \quad (1)$$

where N_H , N_0 are the densities of negative hydrogen ion and neutral atom, respectively; E_- is the binding energy of the additional electron in the negative hydrogen ion = 0.754 eV; T_e is the electron temperature, and

$$\lambda^3 = 2(2\pi\hbar^2/mkT_e)^{3/2}.$$

It was suspected that the actual mechanism for the production of H^- from the NaH plasma was the process of dissociative attachment. Therefore, we proposed to measure dissociative attachment cross sections for LiH, the simplest of alkali hydrides, in a systematic fashion. In the following we will describe the results of this research.

The production of H^- from LiH was studied by two methods: a) molecular beam method and b) solid target method. They are given below.

a) Molecular beam method:

LiH is commercially obtained in a powdered form. Therefore, its molecular beam was formed by heating this powder in the crucible described in Section II of this report. Since the LiH is very hygroscopic, it was always handled in the atmosphere of dry N_2 inside a transparent box through plastic gloves.

Alkali hydrides, when heated to the temperatures that are sufficient to produce a decent molecular beam, dissociate into alkali atoms and H_2 . However, there is a method first developed by Rothstein¹¹ and later applied by Ramsay and

his co-workers¹² for the generation of stable LiH beams. This method involves a careful heating of the crucible. First, the crucible filled with LiH powder is heated to a temperature of about 500K in the vacuum. This heating is done for about 24 hrs. As soon as this heating is started, the background pressure in the vacuum chamber rises from about 10^{-8} Torr to about 10^{-6} Torr. However, after about 24 hrs heating this pressure drops down to 10^{-8} Torr. At that point the temperature is increased once again to about 650K. The background pressure rises. After about 8 hours heating the pressure reduces back to 10^{-8} Torr. The temperature of the crucible is then increased to approximately 800K. This is just below the temperature at which a steady molecular beam is generated. If the temperature is increased too rapidly or in excess of 900K, the beam becomes extremely erratic.

The first thing that we did was to mass analyze the contents of the molecular beam. In order to do this, we changed the various biases in our apparatus so that we could detect positive ions instead of negative ions for which we are normally set up. However, the geometry of observation remained the same as described in Section II. Figure 5 shows a mass scan. We see masses at 1, 16, 42 and 43 amu. There are bumps in the wings of 1 amu peak which we associate with LiH^+ . The present quadrupole mass spectrometer can not resolve masses whose difference is less than 1 amu. Moreover, near 1 amu the resolution is quite poor. Therefore, the peak at 1 amu can be a mixture of H^+ , Li^+ , and LiH^+ . Peaks at 16, 42 and 43 amu are suspected to be polymers of LiH. It is a polar molecule. Such molecules are known to form polymers very efficiently. It is also clear from the Fig. 5 that there are more polymers in the beam than are LiH^+ . This fact is quite disturbing because the dissociative attachment to these polymers can take place and the interpretation of data can be quite erroneous.

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Fig. 5



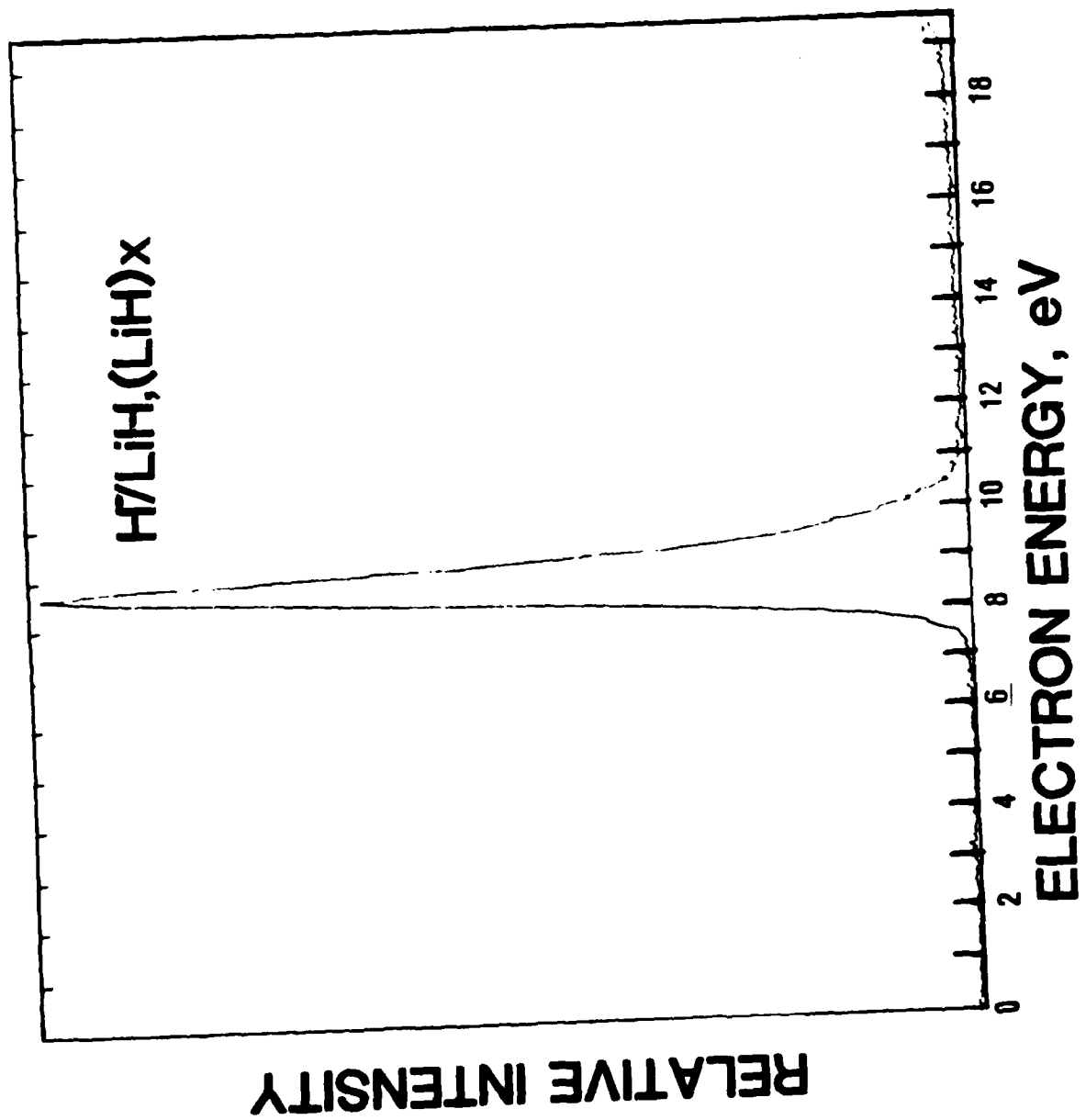


Fig. 6

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The instrument was then changed to the mode for studying negative ions generated by the dissociative attachment. The mass spectrometer was set to detect H^- . The energy of the electron beam was varied from 0 eV to 20 eV. Figure 6 shows the variation of H^- signal as a function of incident electron energy. It is seen that at 8.26 eV there is a peak in the production of H^- . This peak does not coincide with the peak for H^- production from H_2 . Thus, H^- signal observed here is not from H_2 . It is either resulting from the dissociative attachment with LiH or with its polymers $(LiH)_x$ where x is a number higher than 1.

We have not developed a method yet which could be applied for the determination of absolute values of cross sections for those molecules whose beams have to be produced by heating the substance in the crucible. Therefore, cross sections for H^- production from LiH and/or $(LiH)_x$ can not be measured. However, from our experience we can say that these cross sections are quite high: roughly equal to 10^{-17} cm^2 . The signal shown in Fig. 6 is the result of one scan at 10^{-8} amp. e-beam current and with very low pressure molecular beam density. Theoretical calculations about the potential energy surfaces in $(LiH)^-$ would have aided in verifying whether the H^- signal seen in Fig. 6 is from LiH or $(LiH)_x$. However, such calculations are not available at present.

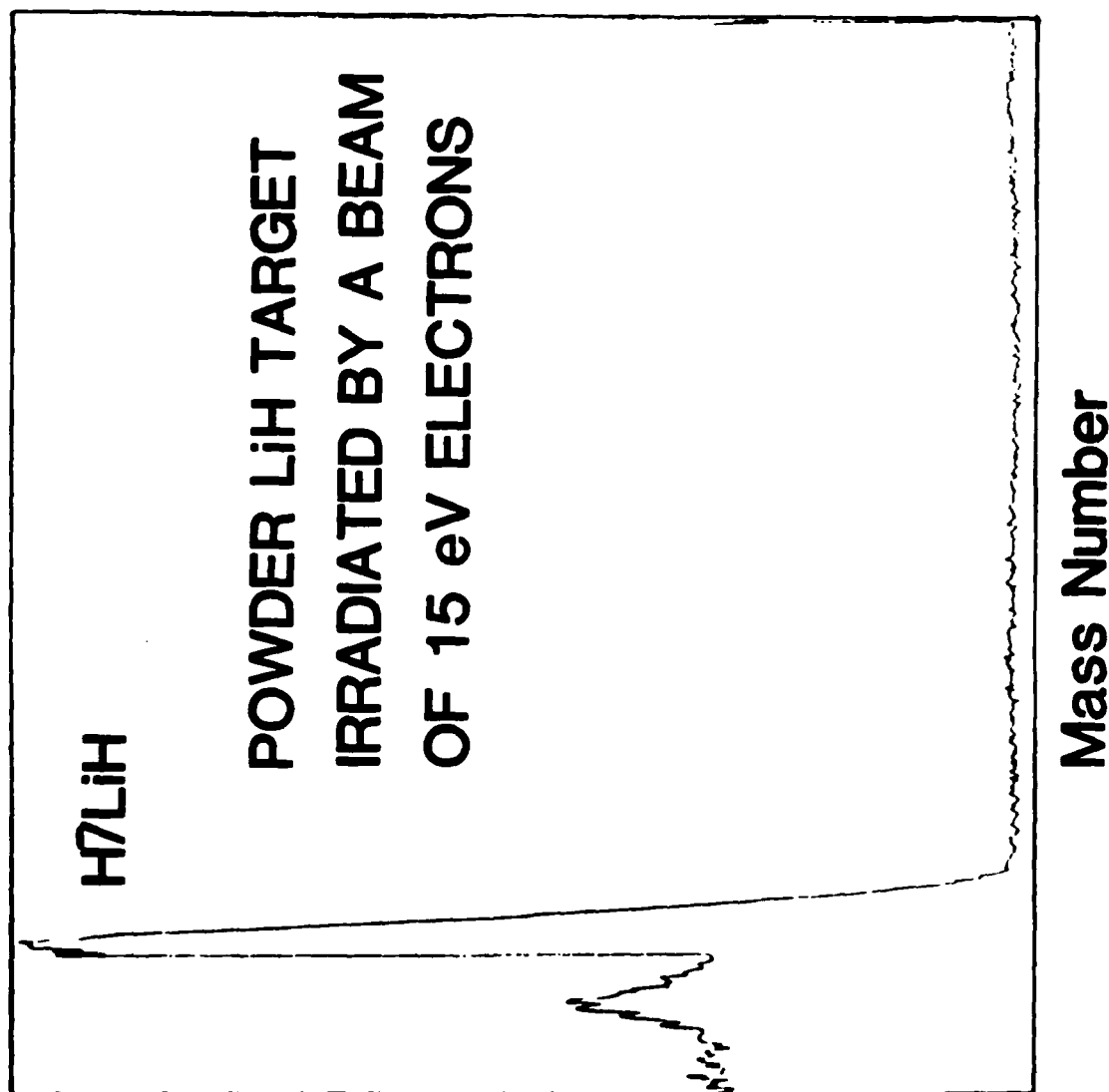
b) Solid target method:

As mentioned in the beginning of the discussion for LiH the motivation for performing this research was generated by the experiment done by Wong and his co-workers¹⁰ where they irradiated a solid NaH target by a CO_2 laser and observed very large signal of H^- . We felt that if LiH powder was irradiated by a beam of electrons it should produce the same effect. In order to accomplish this we put the LiH powder in a molybdenum wire cage and suspended it inside the solenoid (Fig. 3) in such a way that it crossed the electron beam. The electron beam, upon

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Relative Intensity

FIG. 7



collision with the LiH powder, generated H^- which were monitored by the present experimental arrangement as shown in Fig. 3. Figure 7 shows H^- signal from this plasma. It is seen that only H^- is produced and no other kind of ion is seen. In the present case the energy of e-beam was chosen to be 15 eV and the electron beam current was 2.7×10^{-6} amp. The signal of H^- ions was very strong. Work in this direction is in progress. Since the present research is funded this year too we will further explore this method for generating H^- beam.

H₂O: Although dissociative attachment process in H_2O has been investigated by several workers in the past absolute values of cross sections have not been measured by the electron beam method. However, from the swarm data it is known that these cross sections are large. Therefore, H_2O can be a candidate for the generation of H^- beams. We employed the relative flow method described in Section II to measure absolute values of cross sections for the production of H^- and O^- from H_2O . Figures 8 and 9 show H^-/H_2O and O^-/H_2O cross sections, respectively. The peak value 6.5×10^{-18} cm² for H^-/H_2O process is large and should be considered for the generation of H^- beams.

HCl: It is known that HCl has high values of cross sections for the production of Cl^- and H^- . We followed the technique described in the previous pages for the measurements of these cross sections. They are presented in Fig. 10 and 11, respectively. These are the first beam-beam measurements and provide accurate values of cross sections.

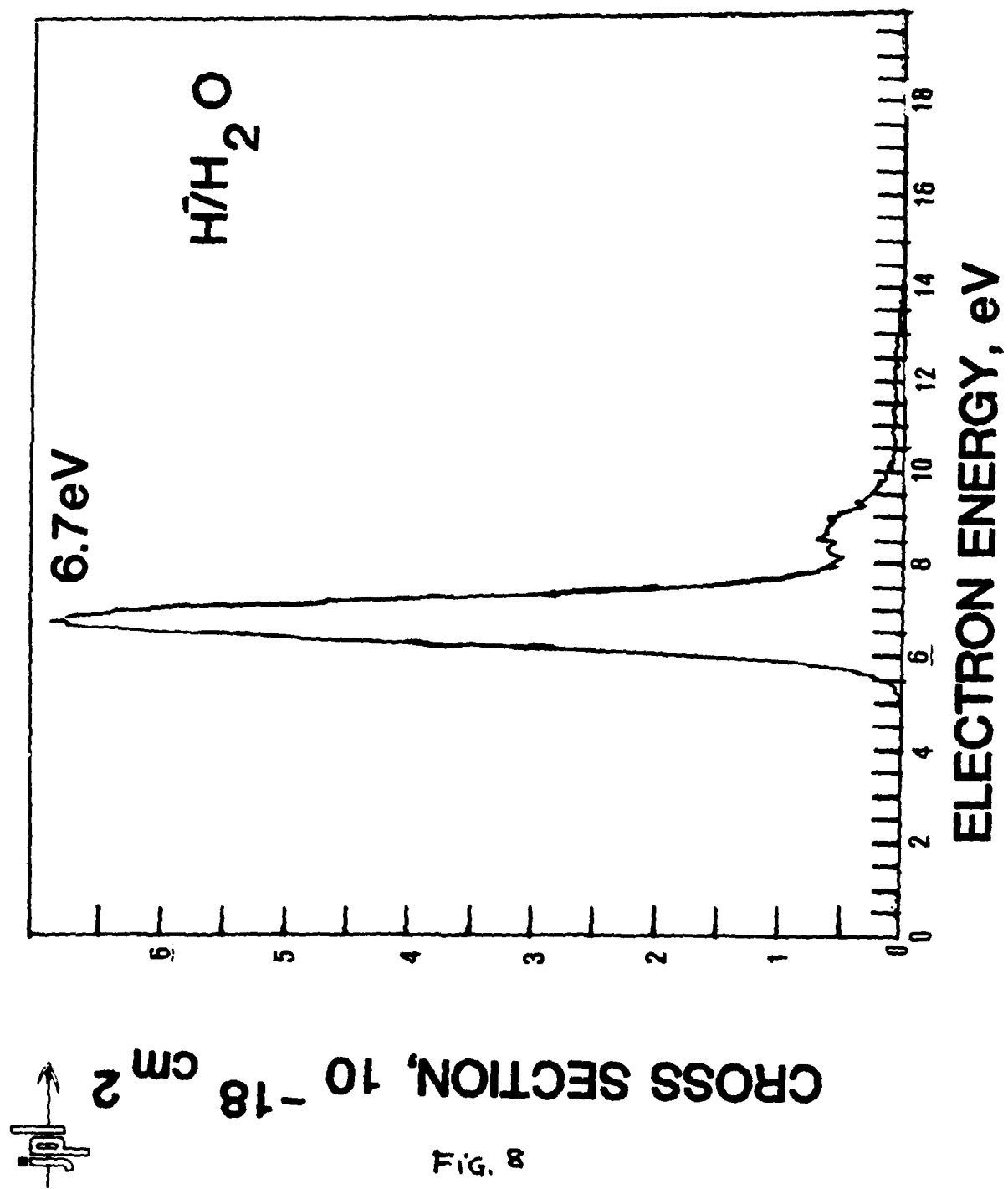


Fig. 8

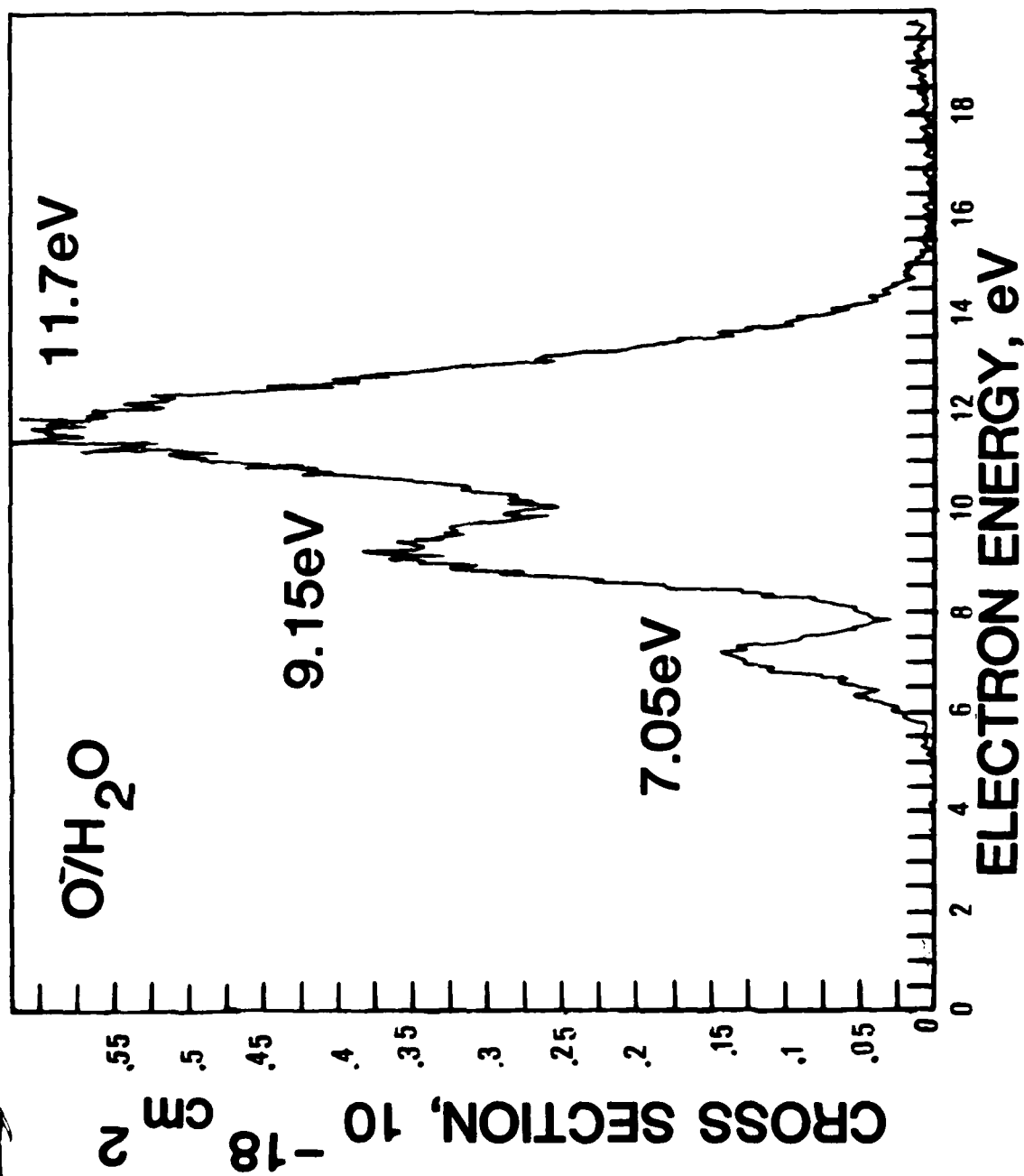


Fig. 9

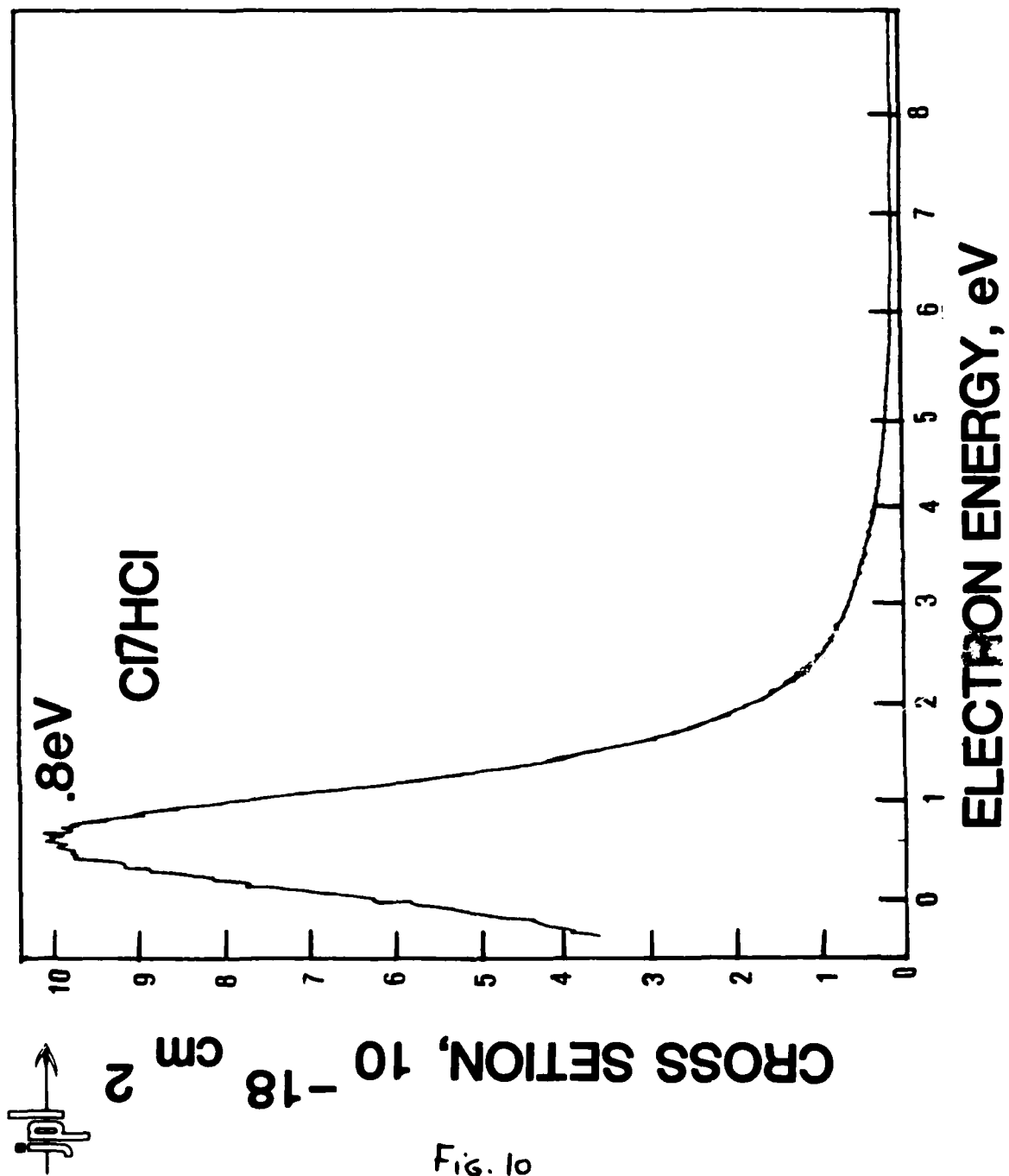


Fig. 10

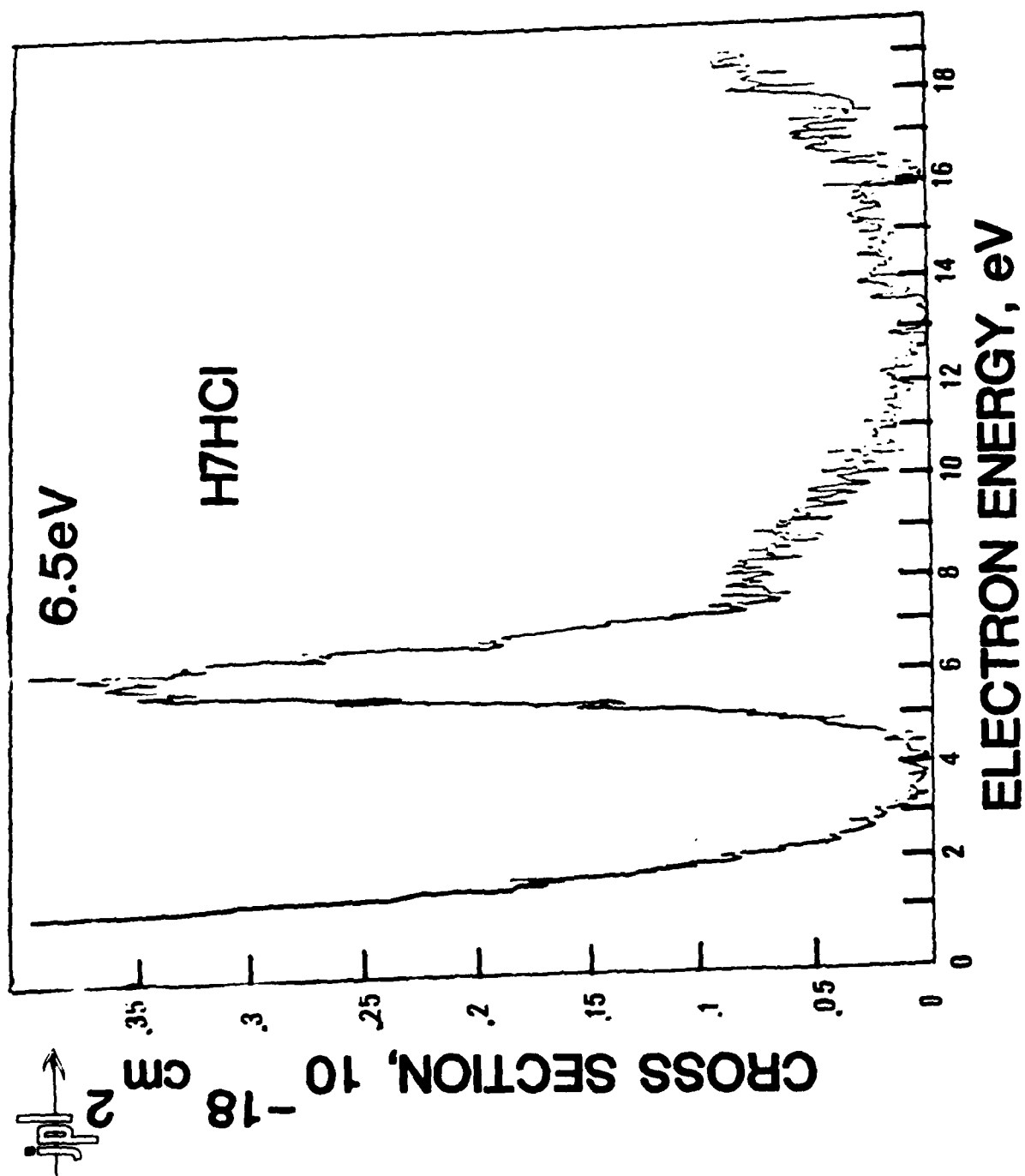


FIG. 11

IV. DOUBLE e-BEAM TECHNIQUE FOR THE STUDY OF DISSOCIATIVE ATTACHMENT FROM VIBRATIONALLY EXCITED STATES

During the course of present research a new technique was developed for studying the process of dissociative attachment from vibrationally excited states of molecules. It has been known from previous studies¹³ that the cross sections for dissociative attachment in some molecules increase by many orders of magnitude when they are vibrationally excited. For the purpose of generation of H^- the double beam arrangement may be useful. This technique has been described in detail in a preprint #3 by Srivastava and Orient and is attached here with this report. We are at present using this technique to measure cross sections for HCl and H_2O . Since the funding for this research is continuing the results will be applied in the fabrication of a H^- source.

REFERENCES

1. L. Vuskovic, S. K. Srivastava and S. Trajmar, J. Phys B: Atom. Molec. Phys. 11, 1643 (1978).
2. G. J. Schulz and R. K. Asundi, Phys. Rev. 158, 25 (1967).
3. D. Rapp and D. D. Briglia, J. Chem. Phys. 43, 1980 (1965).
4. D. Rapp and P. Englander-Golden, J. Chem. Phys. 43, 1464 (1965).
5. K. Stephan, H. Hellm and T. D. Mark, J. Chem. Phys. 73, 3763 (1980).
6. T. C. Ehlert, J. Phys. E3, 237 (1970).
7. G. J. Schulz, Phys. Rev. 128, 178 (1962).
R. K. Asundi, R. K. Craggs and M. V. Kurepa, Proc. Phys. Soc. London, 82, 967 (1968).
8. S. K. Srivastava, A. Chutjian and S. Trajmar, J. Chem. Phys. B: Atom. Molec. Phys. 11, 1643 (1978).
9. K. H. Shoenbauch, G. Schalfer, E. E. Kunhardt, M. Kristiansen, L. L. Hatfield and A. H. Guenther, private communication.
10. A. Y. Wong, J. M. Dason, W. Gekelman and Z. Lucky, App. Phys. Lett. 25, 579 (1974).
11. E. Rothstein, Ph.D. Thesis, UCLRL [Published as a document of Lawrence Radiation Laboratory, #UCRL-17948 (1968)].
12. R. R. Freeman, A. R. Jacobson, D. W. Johnson and N. F. Ramsey, J. Chem. Phys. 63, 2597 (1975).
13. M. L. Allen and S. F. Wong, Phys. Rev. Lett. 41, 1791 (1978).

V. FIGURE CAPTIONS

- Figure 1. Photograph of the experimental arrangement.
- Figure 2. Photograph of the high temperature furnace.
- Figure 3. Schematic diagram of the dissociative attachment spectrometer.
- Figure 4. Relative efficiency of the detection system as a function of mass.
- Figure 5. A mass spectrometer analysis of the contents in the LiH beam.
- Figure 6. Variation of H^- signal from the LiH beam as a function of electron energy.
- Figure 7. H^- signal generated by heating LiH powder by an e-beam.
- Figure 8. Cross sections for the production of H^- from H_2O .
- Figure 9. Cross sections for the production of O^- from H_2O .
- Figure 10. Cross sections for the production of Cl^- from HCl .
- Figure 11. Cross sections for the production of H^- from HCl .

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PRODUCTION OF NEGATIVE IONS BY DISSOCIATIVE ELECTRON ATTACHMENT TO SO_2

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ABSTRACT

Dissociative electron attachment cross section measurements for the production of O^- , S^- , and SO^- have been performed utilizing a crossed target SO_2 molecule beam-electron beam geometry. The relative flow technique is employed to determine the absolute values of cross sections. The attachment energies corresponding to various cross section maxima are: 4.30, 7.1 eV for O^-/SO_2 ; 4.0, 7.5, 8.9 eV for S^-/SO_2 ; and 4.7, 7.5 eV for SO^-/SO_2 .

I. INTRODUCTION

Dissociative electron attachment cross sections for the production of S^- , O^- and SO^- from SO_2 are not known. These cross sections are of particular interest in the modeling of Jupiter-Io's atmosphere¹ and of plasma of diffuse discharge switches.² SO_2 is also a source of sulphur ions in the pulsed ion lasers.³ The above applications motivated us to measure the dissociative electron attachment cross sections for SO_2 .

In the present paper we describe a new instrument (which we have recently fabricated to study the attachment processes in the various gases of interest) and its use in the determination of cross sections for SO_2 . We also describe an extension of our relative flow technique⁴ for the determination of absolute cross sections for dissociative electron attachment.

II. EXPERIMENTAL APPARATUS AND METHOD

A schematic diagram of the apparatus is shown in Fig. 1. It utilizes a crossed electron beam-molecular/atomic beam collision geometry. In the case of gases the beam of atoms or molecules is produced by flowing the gas through a capillary array. Alternatively, in the case of species which are solids or liquids at room temperature an electron bombarded oven or a resistance heated oven⁵ is utilized to produce the target beam. The beam of electrons is generated by heating a pure tungsten filament. The electrons are first extracted from the filament and are then accelerated or decelerated by three cylindrical lenses. This beam is collimated by the help of an axial \vec{B} field which is produced by a solenoid within which the electron gun and a Farady cup are housed. The solenoid produces the \vec{B} field of the order of 200 gauss.

The present beam of electrons is energy unselected. An energy profile of this beam was obtained by utilizing the retarding potential on the Faraday cup.

It is found that the full width at half maximum (FWHM) is approximately 300 meV. The energy of the electrons is varied by changing the bias on the filament with respect to the last electrode of the electron gun. This electrode is kept at ground (earth) potential. It was found that the beam current, as measured by the Faraday cup, remained constant as the energy of the beam was changed from 0.5 eV to about 10 eV which is the energy range of the present interest. Although the energy of the electron beam can be obtained by recording the filament bias voltage, the contact potentials at various surfaces tend to change it from its actual value. In the present work the energy of the beam was calibrated by utilizing the previously measured peak values of electron attachment energies for H^-/H_2 ,⁶ O^-/O_2 ⁷ and O^-/CO_2 .⁸ It was found that the filament bias voltage needed a correction of +0.5 volts to get the true energy of the electron beam.

The negative ions produced by attachment of electrons to the target molecules are extracted out of the \vec{B} field by two parallel molybdenum wire meshes between which a voltage is applied. This voltage produces a homogeneous electric field with a gradient of 3 to 10 V/cm at the target. The direction of the field is normal to both electron beam and molecular beam. One grid is biased negative with respect to the ground and the other positive. The molecular beam is kept at ground potential. It was found that this arrangement did not disturb the electron beam. The efficiency of extraction of ions was measured by changing the extracting electric field from 0 up to 10 V/cm. It was found that by increasing the electric field strength, the detected ion intensity increased rapidly in the beginning. However, at about 3 eV and above the ion intensity became almost constant as a function of the field strength. This indicated that the measured ion current did not depend on the initial energy and angular distribution of the ions. All our measurements were performed in this region of extracting voltage.

The extracted negative ions are accelerated from 0 to about 200 V/cm and focused at the entrance aperture of a quadrupole mass spectrometer by an ion lens (Fig. 1). This mass spectrometer can measure up to about 80 amu and has a resolution of approximately 1 amu. The mass analyzed ions are accelerated by a 3.2 KV potential and are detected by a spiraltron multiplier. Each negative ion is counted as an event by a multichannel scaler.

A vacuum of about 10^{-8} Torr was obtained when the gas forming the molecular beam was not flowed into the vacuum chamber. However, the pressure rose to about 10^{-7} Torr when the molecular beam was on.

The procedure for obtaining the resonance energies is as follows. First, the mass spectrometer is set to detect the mass of interest. Then, the electron energy is varied. The output signal from the spiraltron is recorded by a multichannel scaler as a function of electron energy. This process is repeated several times until sufficient signal to noise ratio is obtained. The variation of ion intensity as a function of energy usually shows a maximum.

The relative intensities of negative ions of various masses give the values of relative cross sections. These cross sections, in turn, are the measures of relative efficiencies for the production of the various species by dissociative attachment. However, in order to get the true values of relative intensities one has to know the values of mass dependent transmission efficiencies of the ion optics, the quadrupole mass spectrometer and the charged particle detector. The determination of these efficiencies will be described at the end of this section.

In order to obtain the absolute values of the cross sections, the relative flow technique¹ developed in our laboratory for collision cross section measurements was utilized. This technique employs a measurement of the ratio of the intensity of the negative ions of the unknown species (for example, O^-/SO_2^- ,

S^-/SO_2 , SO^-/SO_2) to that of from O^-/O_2 . At the same time, the flow rates behind the capillary array⁴ are measured. First, the gas (AB of Eq. 1) whose dissociative attachment cross section has to be measured is flowed through the capillary array and a beam is formed. The negative ion intensity $I(B^-)$ is then measured. Subsequently, the gas AB is turned off and O_2 is flowed through the capillary array. The negative ion current $I(O^-)$ is again recorded. Providing that the measurement is performed under the conditions of molecular flow through the capillary array, the following relation is used to obtain the cross section:

$$\sigma(B^-/AB) = \sigma(O^-/O_2) \frac{I(B^-)}{I(O^-)} \left[\frac{m(O_2)}{m(AB)} \right]^{\frac{1}{2}} \cdot \frac{N(O_2)}{N(AB)} \cdot K \quad (1)$$

where $m(AB)$ and $m(O_2)$ are molecular weights of respective gases, $N(O_2)$ and $N(AB)$ are the flow rates of the two gases through the capillary array and K is a calibration constant which determines the transmission efficiency of the ion optics, quadrupole mass spectrometer and charged particle detector for B^- and O^- .

Calibration constant K for the various masses was experimentally obtained by assuming that the transmission efficiency of the ion optics, quadrupole mass spectrometer and charged particle detector do not depend upon the charge of the particle. Thus, the values of K should be the same for B^+ as for B^- or for O^+ as for O^- . We chose gases whose ionization cross sections are well known. These are $(H^+/H_2)^8$, $(He^+/He)^9$, $(O^+/O_2)^8$, $(Ne^+/Ne)^9$, $(Ar^+/Ar)^9$ and $(Kr^+/Kr)^9$. Utilizing equation (1) and changing in it all negative signs into positive signs one obtains an equation for positive ion cross sections. Since all the quantities in this equation are either known or can be obtained experimentally for the two gases out of the ones mentioned above except K the values of K for various mass numbers ranging from H to Kr can be calculated. We followed this method for

calibrating our instrument. The calibration constant K (relative efficiency) as a function of the mass number is a bell shaped curve shown in Fig. 2. The relative efficiency is increasing with the mass number up to about mass number 45, then it is decreasing at higher mass number. Our results are in agreement with Ehlert's measurements (full curve, Fig. 2).¹⁰ We have checked out results in the case of negative ions using the well known dissociative electron attachment cross sections of $[H^-/H_2]^6$ and $[O^-/O_2]^7$. Taking into account our 5% error in measurements, the relative efficiency value in the case of negative and positive ions are equal, i.e., $K(\frac{O^-}{H^-}) = K(\frac{O^+}{H^+})$.

The contribution of the background scattering (both direct beam contribution and scattering by the background gas) to the scattering from the target gas beam is measured by providing an alternate leak to the vacuum chamber (see Fig. 1). The flow to the chamber is switched from the capillary array to the alternate gas inlet and the proper background pressure for the desired gas is established. The mass selected beam intensity is then measured as a function of the electron beam energy. It is found that the maximum value of the background scattering is about 5%. Thus, by using the side leak we have obtained background signal to correct the final results reported in the next section.

III. RESULTS

The measured dissociative electron attachment cross sections of $[O^-/SO_2]$, $[S^-/SO_2]$ and $[SO^-/SO_2]$ as a function of the electron beam energy are shown in Figs. 3(a), 3(b), and 3(c). In the case of $[O^-/SO_2]$ there are two peaks in the cross section curve at 4.3 ± 0.05 eV and 7.1 ± 0.05 eV respectively. $[S^-/SO_2]$ has three peaks at 4.0 ± 0.05 eV, 7.5 ± 0.1 eV and 8.9 ± 0.1 eV respectively. The second and the third peaks are smaller by about one order of magnitude than the first peak. In the case of $[SO^-/SO_2]$ there are two peaks at 4.7 ± 0.05 eV and 7.5 ± 0.2 eV

respectively. The position of the second peak is not well defined and its cross section value is quite low compared to the first peak. For the case of $[O^-/SO_2]$, $[S^-/SO_2]$ and $[SO^-/SO_2]$ the negative ion signal intensity does not change as the ion extracting electric field strength between the collision region and ion optics (Fig. 1) is varied from 20 to 200 V/cm. This suggests that these negative ions are stable.

The negative ion intensity at mass number 32 can be S^- or O_2^- . However, S^- has two isotopes. One has a mass number 32 and the other has 34. The lighter mass has an abundance of 95% while the heavier one has a value of 4.2%. We monitored the heavier mass number and found that the ratio of the two mass peaks is supportive of S^- at mass number 32 rather than O_2^- .

Table I presents the measured $\sigma[O^-/SO_2]$, $\sigma[S^-/SO_2]$, and $\sigma[SO^-/SO_2]$. In Table II we have summarized various sources of errors that contribute to the total error in the present results. The total error in the measurement of the ratio $\sigma(B^-/AB)/(O^-/O_2)$ (Eqn. 1) was about 13%. The absolute value of $\alpha(B^-/AB)$ is obtained by multiplying this ratio by the value of $\alpha(O^-/O_2)$. The error of $\sigma(O^-/O_2)$ has been estimated to be about 5% arrived at by comparing the various values reported in the literature.^{7,11} Therefore, the present values of $\sigma(B^-/AB)$ are uncertain by about 20%.

IV. ACKNOWLEDGEMENT

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REFERENCES

1. A. F. Cheng, The Astr. Jour. 242, 812 (1980).
2. K. H. Shoenbach, G. Schaefer, E. E. Kunhardt, M. Kristiansen, L. L. Hatfield, and A. H. Guenther, private communication.
3. J. Marling, IEEE Jour. Quant. Electr. QE-14, 4 (1978).
4. S. K. Srivastava, A. Chutjian and S. Trajmar, J. Chem. Phys. 63, 2659 (1975).
5. L. Vusković, S. K. Srivastava and S. Trajmar, J. Phys. B: Atom. Molec. Phys. 11, 1643 (1978).
6. G. J. Schulz and R. K. Asundi, Phys. Rev. 158, 25 (1967).
7. D. Rapp and D. D. Briglia, J. Chem. Phys. 43, 1980 (1965).
8. D. Rapp and P. Englander-Golden, J. Chem. Phys. 43, 1464 (1965).
9. K. Stephan, H. Helm and T. D. Mark, J. Chem. Phys. 73, 3763 (1980).
10. T. C. Ehlert, J. Phys. E3, 237 (1970).
11. G. J. Schulz, Phys. Rev. 128, 178 (1962);
R. K. Asundi, R. K. Craggs and M. V. Kurepa, Proc. Phys. Soc. London, B2, 967 (1968).

Table I. Dissociative Attachment Cross Sections for the Following Reaction
 $e + SO_2 \rightarrow O^-, S^-, SO^-$

Electron Energy (eV)	Cross Sections		
	$\sigma(O^-)$ ($\times 10^{-18} \text{ cm}^2$)	$\sigma(S^-)$ ($\times 10^{-18} \text{ cm}^2$)	$\sigma(SO^-)$ ($\times 10^{-18} \text{ cm}^2$)
2.5	.01	.0	.0
3.0	.10	.013	.02
3.1	.16	.019	.0
3.2	.22	.034	.03
3.3	.36	.056	.03
3.4	.58	.079	.16
3.5	.89	.122	.16
3.6	1.34	.167	.36
3.7	2.20	.225	.54
3.8	3.16	.276	.84
3.9	4.38	.298	1.41
4.0	5.58	.313	2.05
4.1	6.92	.310	3.27
4.2	7.52	.295	4.58
4.3	8.08	.271	6.94
4.4	8.02	.246	8.51
4.5	7.22	.231	10.10
4.6	6.48	.191	10.80
4.7	5.48	.162	10.98
4.8	4.69	.164	10.53
4.9	3.79	.131	9.07
5.0	3.14	.114	7.76
5.1	2.56	.091	5.86
5.2	1.90	.065	4.84
5.4	1.12	.044	2.80
5.6	.69	.028	1.21
5.8	.45	.013	.62
6.0	.43	.015	.39
6.2	.81	.008	.33
6.3	.86	.018	.46
6.4	1.17	.017	.40
6.5	1.32	.020	.58
6.6	1.59	.022	.44
6.7	1.80	.019	.52
6.8	2.10	.017	.58
6.9	2.33	.025	.41
7.0	2.56	.027	.42
7.1	2.68	.026	.40
7.2	2.41	.030	.42
7.3	2.47	.031	.51
7.4	2.41	.031	.44
7.5	2.14	.036	.51
7.6	1.89	.030	.43
7.7	1.56	.029	.33
7.8	1.33	.027	.28

Table I. (Continued)

Electron Energy (eV)	Cross Sections		
	$\sigma(O^-)$ ($\times 10^{-18} \text{ cm}^2$)	$\sigma(S^-)$ ($\times 10^{-18} \text{ cm}^2$)	$\sigma(SO^-)$ ($\times 10^{-18} \text{ cm}^2$)
7.9	1.06	.016	.21
8.0	.93	.015	.21
8.1	.76	.015	.13
8.2	.61	.015	.11
8.3	.50	.013	.05
8.4	.35	.013	.0
8.5	.27	.014	.01
8.6	.25	.016	0
8.7	.14	.026	
8.8	.09	.021	
8.9	.07	.030	
9.0	.04	.027	
9.1	.04	.026	
9.2	.02	.017	
9.3	.01	.015	
9.5	.01	.002	

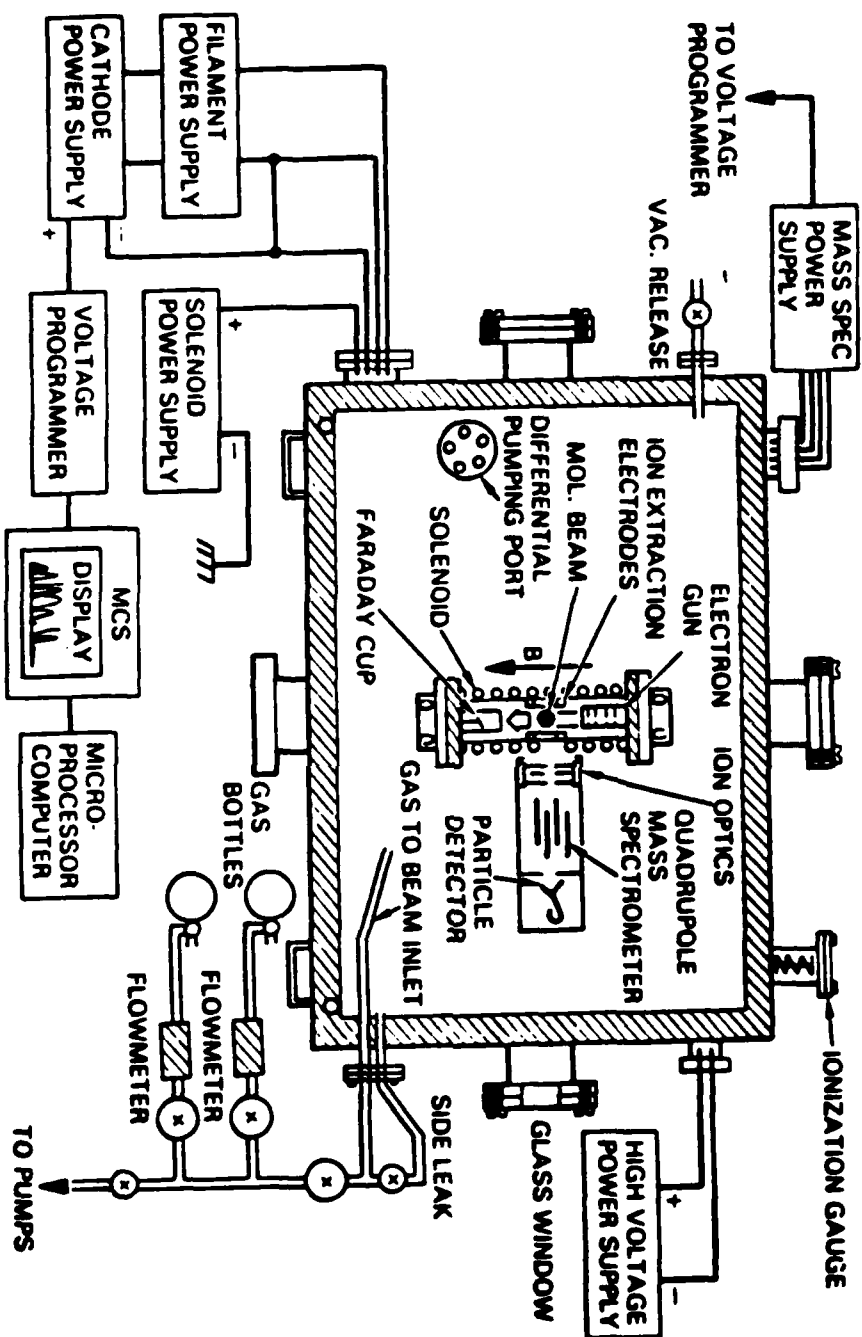
Table II. Sources of Errors that Contribute to the Total Error
in the Measure of the Ratio $\sigma[B^-/AB]/\sigma[O^-/O_2]$.
The Various Quantities are Defined in Eqn. (1)

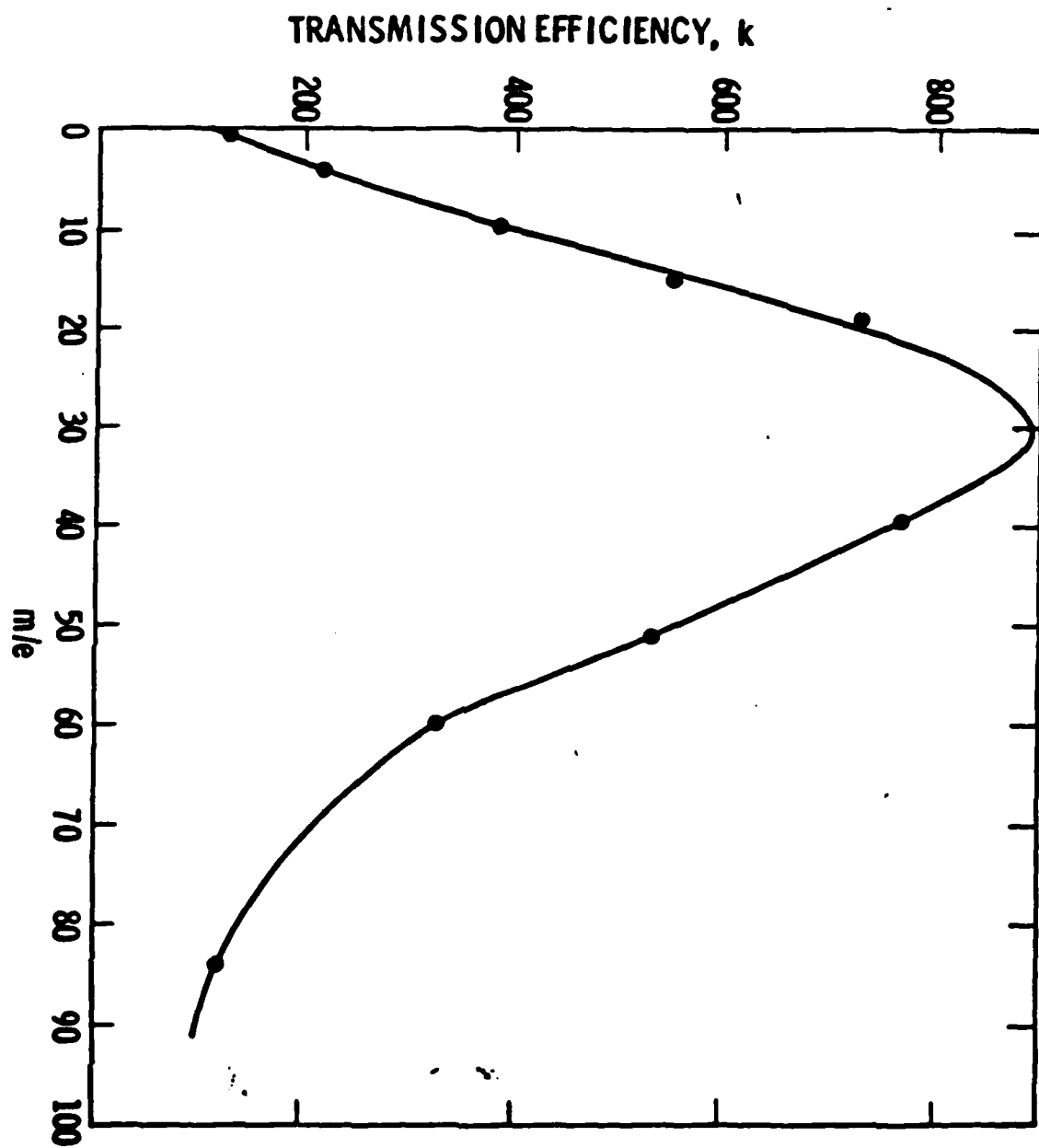
(1)	Error in the measurement of flow rate $N(O_2)/N(AB)$	$\pm 3\%$
(2)	Estimated error in the ratio $I(B^-)/I(O^-)$	$\pm 5\%$
(3)	Estimated error due to the change in the incident electron-beam current	$\pm 2\%$
(4)	Estimated error in the calibration constant K	$\pm 5\%$
		<hr/>
Total		$\pm 13\%$

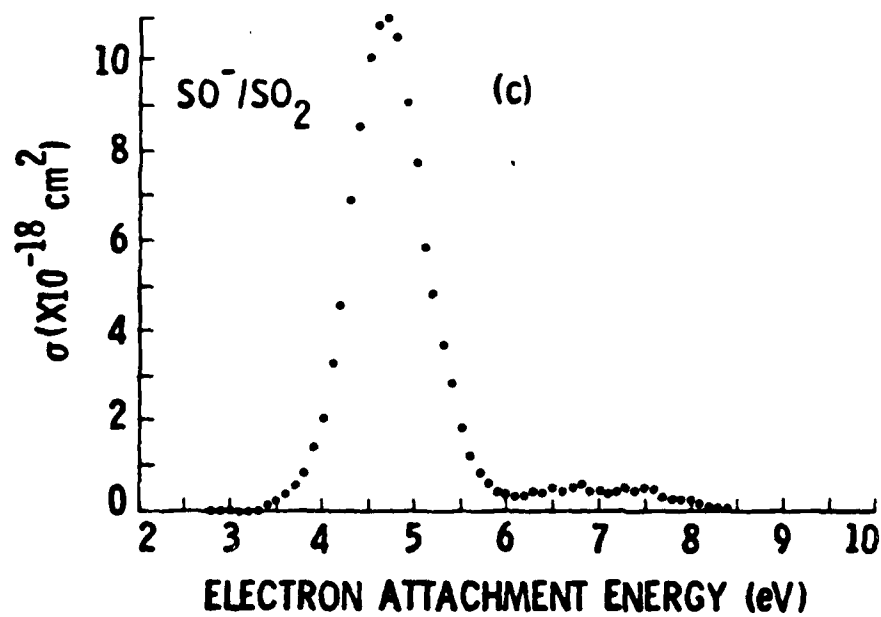
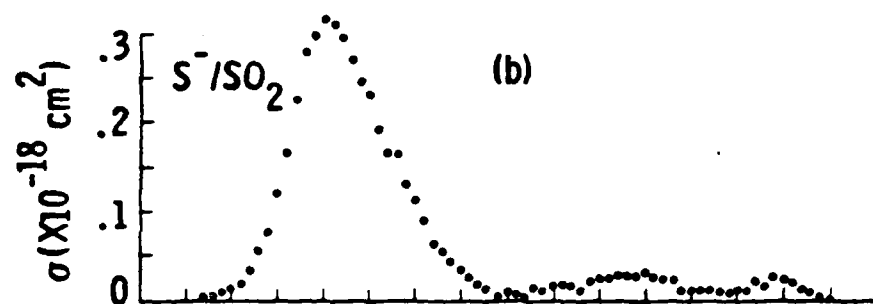
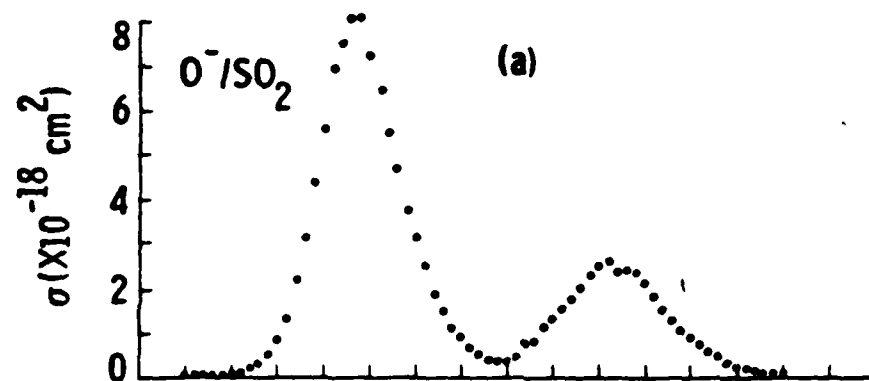
FIGURE CAPTIONS

- Figure 1. Schematic diagram of the apparatus.
- Figure 2. Transmission efficiency curve for the quadrupole mass filter, K plotted as a function of m/e . K at $m/e = 0$ is taken as 100. Points are our measurement values. Continuous curve is Ehler's measurement.¹⁰
- Figure 3(a). Dissociative electron attachment cross section for O^-/SO_2 as a function of the electron beam energy.
- Figure 3(b). Dissociative electron attachment cross section for S^-/SO_2 as a function of the electron beam energy.
- Figure 3(c). Dissociative electron attachment cross sections for SO^-/SO_2 as a function of the electron beam energy.

DISSOCIATIVE IONIZATION AND ATTACHMENT SPECTROMETER (DIMENSIONS NOT TO SCALE)







A DOUBLE e-BEAM TECHNIQUE FOR COLLISION STUDIES FROM EXCITED STATES:

APPLICATION TO VIBRATIONALLY EXCITED CO₂^{*}

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ABSTRACT

We describe a new technique which utilizes two beams of electrons to study the electron scattering from the excited states of atoms and molecules. The capability of the technique is specifically demonstrated by applying it to the process of dissociative electron attachment with vibrationally excited CO_2 .

Electron scattering from the excited states of atoms and molecules plays an important role in high temperature plasmas, gas discharges and aurorae. However, the cross sections for this process are not known accurately, principally because it is difficult to produce a sufficiently high number density of excited-state species to enable the collision studies. In the past, tunable lasers have been employed for excitation but for various reasons only a limited number of species could be investigated in this manner.

We present here a technique which utilizes two beams of electrons for studying the scattering of electrons from excited states. A schematic diagram illustrating the principle of the technique is shown in Fig. 1. It employs a crossed electron beam-target beam geometry. The target beam is produced by flowing the gas under study through a capillary array or a hypodermic needle. This beam is crossed at 90° by two beams of electrons travelling in opposite directions. The electron energies of the two beams can be varied independently. Each of the electron beams is collimated by a magnetic field (B-field) produced by a solenoid. One beam (beam #2) is used to excite the target species to its various excited states and the other beam (beam #1) is utilized to observe the scattering from the excited states. These beams of electrons are energy unselected. Their energy profiles were obtained by utilizing the retarding potential on a Faraday cup. It was found that the full width at half maximum (FWHM) of individual beams was approximately 300 meV. The energy of the electrons is varied by changing the bias on the filament with respect to the last electrode of each electron gun. This electrode is kept at ground (earth) potential. The beam current, as measured by a Faraday cup in a separate experiment, remained constant as the energy of the beam was changed from 0.5 eV to about 20 eV which is the energy range of the present interest. Although the energy of the electron beam can be obtained by recording the filament bias

voltage, the contact potentials at various surfaces tend to change it from its actual value. In the present work the energy of the beams was calibrated by utilizing the previously well known peak values of electron attachment energies for H^-/H_2 , O^-/O_2 and O^-/CO_2 . It was found that the filament bias voltage needed a correction of +0.5 volts to get the true energy of the electron beam. We estimate that after correction the energy of the individual electron beams is accurate to within 0.1 eV. In general, the current in e-beam #1 was $3.6 \times 10^{-8} A$ and in the e-beam #2 it was $0.5 \times 10^{-6} A$. A detailed description of the apparatus is given in Ref. 1. A vacuum of about 10^{-8} Torr was obtained when the gas forming the molecular beam was not flowed into the vacuum chamber. However, the pressure rose to about 10^{-7} Torr when the molecular beam was on. Under these conditions the pressure in the molecular beam is estimated to be less than about 10^{-3} Torr. At this pressure the probability of multiple scattering is negligible.

This technique is quite suitable for studying the process of dissociative electron attachment with rotationally vibrationally excited states of molecules. The cross sections for this process are expected to be quite large. In the past, the rotationally and vibrationally excited states were produced by heating^{2,3,4} the gas under study in a crucible. However, due to practical limitations imposed by high temperatures, only low lying vibrational states were generated. On the other hand, by utilizing a beam of electrons higher vibrational states and even electronic states of the molecules can be populated.

We present here the application of the above technique to the study of dissociative attachment with vibrationally excited states of CO_2 . In dissociative attachment the following reaction takes place:



The O^- ions are produced for certain specific energies of electrons. These ions are extracted out of the interaction region by an electric field of the order of 2 to 3 v/cm applied at 90° to both the electron beam and molecular beam. The ions are then focused at the entrance aperture of a quadrupole mass spectrometer by ion lenses.

The mass spectrometer was set to detect O^- . The procedure for obtaining the resonance energies and relative values of cross sections was as follows. First, the electron beam #2 (Fig. 1) was turned off. Then, the electron energy of the beam #1 was varied. The output signal from the mass spectrometer was recorded by a multichannel scaler as a function of electron energy. An example of the variation of the O^- signal as a function of electron energy thus obtained is shown in Fig. 2a. In the energy region of 0 to 20 eV, six intensity peaks were seen. These lay at 4.4 ± 0.1 , 8.2 ± 0.1 , 13.0 ± 0.2 , 15 ± 0.5 , 16.9 ± 0.2 and 19.4 ± 0.2 eV respectively. The first two were the most intense ones. In the second step, the electron beam #2 (Fig. 1) was also turned on. Its energy was fixed at 1.2 eV, based upon knowledge that at about this energy the vibrational excitation cross section for CO_2 are largest⁵ ($\approx 10^{-16}$ cm²). Thus, the electron beam #2 populates the vibrationally excited states of CO_2 . The energy of the electron beam #1 was again varied from 0 eV to 20 eV. The resulting spectrum is shown in Fig. 2(b). We found that the intensities of the spectral features were enhanced and the intensity of the resonance peak at 4.4 eV was larger than that at 8.2 eV. This shows that the cross sections for the dissociative attachment at 4.4 eV increase when CO_2 is vibrationally excited. This observation was further supported by the increase in the O^- intensity when beam #1 (Fig. 1) was fixed at 4.4 eV and beam #2 was swept from 0 eV to 5 eV. The resulting spectrum is shown in Fig. 3. It is seen in this figure that when electron beam #2 has an energy of about 1.0 eV the O^- signal goes

through a maximum. This is in agreement with Boness and Schulz⁵ who found a maximum in the vibrational excitation at about 1.0 eV.

O⁻ production from CO₂ has been studied in the past by several researchers.^{2,3,6} Mainly, these studies have been related to the measurement of cross sections a) at room temperature, b) at higher temperatures, and c) the measurement of kinetic energy of O⁻ fragments. In general, the following conclusions have been drawn: i) there are three peaks³ for the O⁻ intensity at 4.4 eV, 8.2 eV and 13.0 eV respectively, ii) the ratio of intensities of these peaks depends on the temperature² of CO₂, showing that the cross sections change with the vibrational population in the ground state. Furthermore, the thresholds for the formation of O⁻ are also temperature dependent,² with shift toward lower energies as the temperature increases, and iii) vibrationally excited CO is formed as a result of dissociation.

The present work shows (Fig. 2a) that in addition to the three O⁻ peaks observed before, there exist three additional peaks. The ratio of the intensity of the peak at 8.2 eV to that at 4.4 eV is 3.0 ± 0.1 , which is in excellent agreement with previous measurements.² We also find that when CO₂ is excited by e-beam #2 the intensity of the 4.4 eV feature (Fig. 2b) increases to the extent that the ratio of the 4.4 eV peak to the 8.2 eV one becomes greater than 1.0. This is also in agreement with the previous results. However, the present work does not show any appreciable increase in the intensity of other features, such as a shift² in the threshold value of the excitation or an increase in the intensity of the valley³ between the 4.4 eV and 8.2 eV features. This is contrary to the previous findings^{2,3} which were obtained for vibrationally excited CO₂ populated by heating in a high temperature crucible. In our view the reason for this difference lies in the method of exciting the vibrational modes in CO₂. As shown by Boness and

Schulz⁵ by use of electron impact, principally the asymmetric stretch mode (001) is excited. However, by heating, all the vibrational and rotational modes are excited. The coupling of these states with the CO_2^- states may be different from the single asymmetric stretch mode generated by the electron impact.

In order to fully understand the process of dissociative attachment with CO_2 one needs to know details on the various potential energy surfaces of CO_2^- . There are two previous calculations by Claydon et al.⁸ (INDO SCF theory) and by England et al.⁹ (ab initio SCF calculations). These calculations explain the onset of the 4.4 eV feature very well and assign a $2\pi_u$ state of CO_2^- to be responsible for the O^- production. However, $2\pi_g^+$ state shape resonance, as calculated by Claydon et al., does not accurately account for the threshold or the peak position of the 8.2 eV feature (Fig. 2). A similar situation exists with the higher energy peaks. Our results showing small dependence of cross sections on vibrational excitation indicate that the 8.2 eV feature and the features at higher energies originate from CO_2^- states which are Feshbach resonances, rather than shape resonances. Because the vibrational excitation strongly affects the shape resonances (potential scattering), the dramatic change in the intensity of the 4.4 eV feature ($2\pi_u$ CO_2^- state) takes place. However, the 8.2 eV and higher energy features result from electronic rearrangement in the molecule (Feshbach resonances) and do not depend appreciably upon nuclear motion. Winter¹⁰ has carried out Hartree Fock calculations with large basis sets for some of these higher CO_2^- states. These calculations predict a $2\pi_g$ Feshbach resonance at 8.3 eV. This state has an electronic configuration of $1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 4\sigma_g^2 1\sigma_u^2 2\sigma_u^2 3\sigma_u^2 1\pi_u^4 1\pi_g^3 3s\sigma_g^2 (2\pi_g^-)$. Its parent states are $1,3\pi_g$ whose energies are 9.0 eV and 9.3 eV for the triplet and singlet states respectively.

In conclusion, we find that the double e-beam technique can be successfully

employed for studying the electron scattering from excited states. It has been demonstrated clearly, using CO_2 as an example, that upon selecting proper energies the various vibrational states can be excited, from which the process of dissociative attachment can be studied. This technique may find wide application for certain special types of measurements, and is of immediate interest in this regard.

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REFERENCES

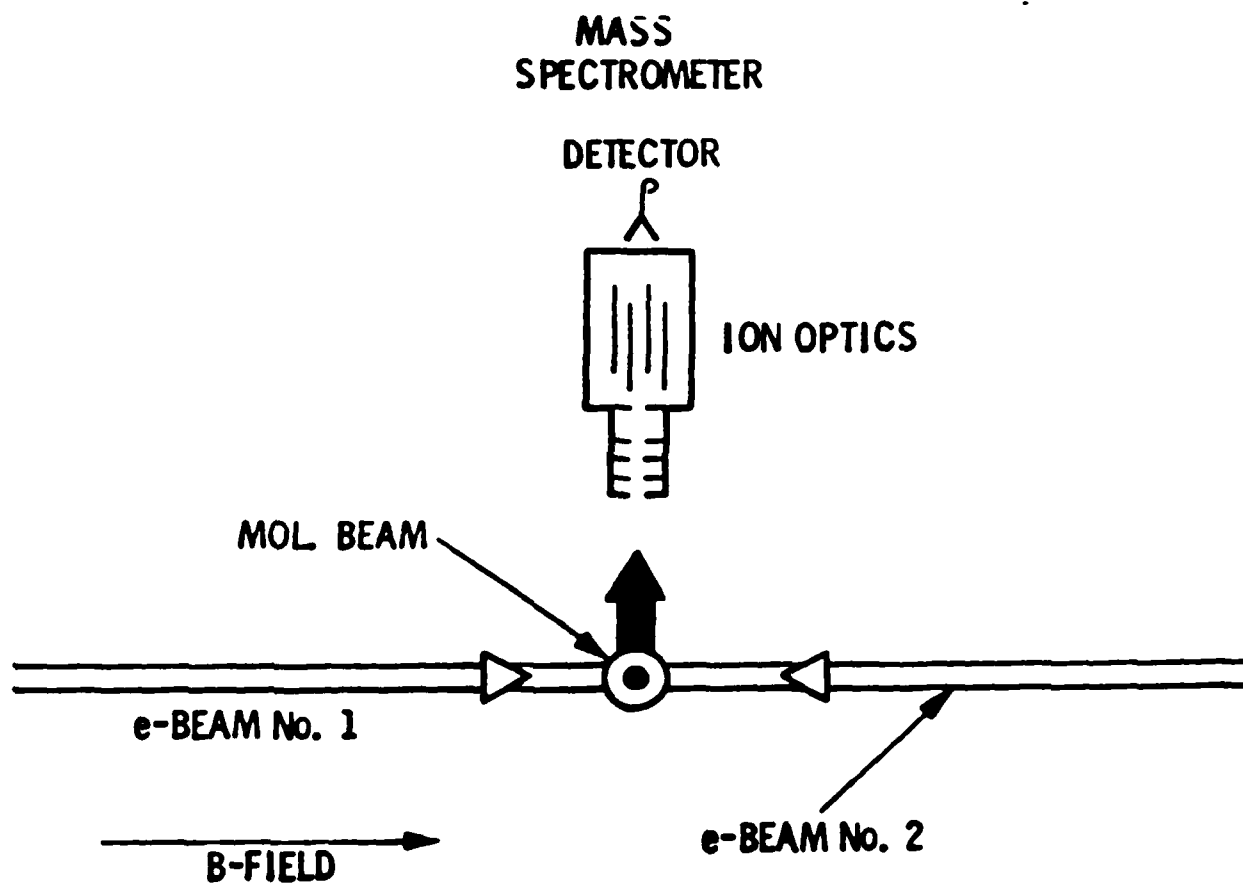
1. O. J. Orient and S. K. Srivastava, submitted for publication in J. Chem. Phys.
2. D. Spence and G. J. Schulz, Phys. Rev., A1 88, 180 (1969).
3. P. J. Chantry, J. Chem. Phys. 57, 3180 (1972).
4. M. L. Allan and S. F. Wong, Phys. Rev. Lett., 41, 1791 (1978).
5. M. J. W. Boness and G. J. Schulz, Phys. Rev. Lett., 21, 1081 (1968).
6. D. Rapp and D. D. Briglia, J. Chem. Phys., 43, 1480 (1965).
7. A. Stamatovic and G. J. Schulz, Phys. Rev. A7, 589 (1973).
8. C. R. Claydon, G. A. Segal, and H. S. Taylor, J. Chem. Phys., 52, 3387 (1970).
9. W. B. England, B. J. Rosenberg, P. J. Fortune and A. E. Wahl, J. Chem. Phys., 65, 684 (1976).
10. N. W. Winter, private communication.

FIGURE CAPTIONS

Figure 1. A conceptual diagram of the double e-beam arrangement.

Figure 2. a) O^-/CO_2 signal as a function of energy of e-beam #1 and e-beam #2 off.
b) O^-/CO_2 signal as a function of energy of e-beam #1 and e-beam #2 fixed at 1.2 eV.

Figure 3. O^-/CO_2 signal with e-beam #1 fixed at 4.2 eV and e-beam #2 swept from 0 to 4 eV.



SCHEMATIC DIAGRAM SHOWING
DOUBLE e-BEAM ARRANGEMENT

